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Synthesis of Phosphonitrilic Plastics and Elastomers for Marine Applications

Horizons Research, Inc.

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Army Materials and Mechanics Research Center

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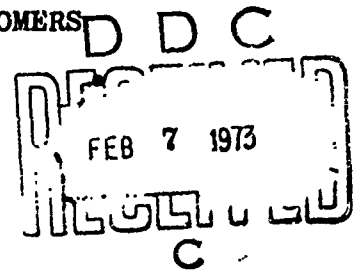


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SYNTHESIS OF PHOSPHONITRILIC PLASTICS AND ELASTOMERS
FOR MARINE APPLICATIONS

December 1972



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P00003

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13. ABSTRACT Eleven different, flame-retardant, relatively inexpensive poly(aryloxyphosphazenes) were prepared. The poly(aryloxyphosphazenes) displayed high flame retardancy in the unfilled, uncured state. Limiting Oxygen Index values varied from 27 to 33 for nonhalogenated materials and from 38 to 65 for halogenated materials. The three poly(aryloxyphosphazenes) tested performed very well in the NBS smoke test and the National Electrical Manufacturers test (ASTM D229). Dielectric properties compared favorably with polyvinyl chloride and polyethylene. Ten of the materials were plastics which were good film formers and most films were flexible, strong and oriented upon drawing. These materials included the $[(C_6H_5O)_2PN]_n$, $[(4-ClC_6H_4O)_2PN]_n$ and $[(3-CH_3C_6H_4O)_2PN]_n$ homopolymers and the $[(4-ClC_6H_4O)_2PN-(2,4-Cl_2C_6H_3O)_2PN]_n$ copolymer. The $[(C_6H_5O)_2PN-(4-C_2H_5C_6H_4O)_2PN]_n$ copolymer was a leathery elastomer. The poly(alkylaryloxyphosphazenes) had wider solubility than $[(C_6H_5O)_2PN]_n$ or the poly(haloaryloxyphosphazenes). In general, the polymers showed good chemical resistance to acids and bases. ✓			

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ABSTRACT

A number of flame-retardant, relatively inexpensive poly(aryloxyphosphazenes) were prepared for use in marine applications. Plastics, damping compounds and elastomers were prepared dependent on the side chains attached to the phosphorus-nitrogen backbone.

The polymerization of hexachlorophosphazene and subsequent derivatization of poly(dichlorophosphazene) were carried out in quantities sufficient to prepare kilogram quantities of many materials. A total of eleven different poly(aryloxyphosphazenes) were prepared, ten were plastics and one was a leathery elastomer. All the plastics were excellent film formers and most films were flexible, strong, and oriented upon drawing. The $[(C_6H_5O)_2PN]_n$, $[(3-CH_3C_6H_4O)_2PN]_n$ and $[(4-ClC_6H_4O)_2PN]_n$ homopolymers and the $[(4-ClC_6H_4O)_2PN-(2,4-Cl_2C_6H_3O)_2PN]_n$ copolymer were particularly noteworthy with respect to orienting upon drawing. The elastomer was a $[(C_6H_5O)_2PN-(4-C_2H_5C_6H_4O)_2PN]_n$ copolymer.

The poly(aryloxyphosphazene) homopolymers and copolymers displayed a high degree of flame retardancy in the uncured, unfilled state. Limiting Oxygen Index (LOI) values varied from 27 to 33 for nonhalogenated materials and from 38 to 65 for halogenated materials. These values qualify all poly(aryloxyphosphazenes) which were prepared as flame retardant according to the generally accepted definition ($LOI \geq 27$).

The three poly(aryloxyphosphazene) plastics which were tested performed quite well in the NBS smoke test and the National Electrical Manufacturers test (ASTM D229). Smoke density values (D_{max}) of 261 and 455 for $[(4-CH_3C_6H_4O)_2PN]_n$ and $[(4-ClC_6H_4O)_2PN]_n$ homopolymers were considered very good and fair, respectively. The $[(C_6H_5O)_2PN]_n$ homopolymer was intermediate in value for D_{max} . The $[(4-ClC_6H_4O)_2PN]_n$ homopolymer was outstanding with ignition and burning times of 136 (T_i) and 4.5 (T_b) seconds in the ASTM D229 test. The $[(C_6H_5O)_2PN]_n$ and $[(3-CH_3C_6H_4O)_2PN]_n$ homopolymers also performed admirably in this test, although lower T_i and higher T_b values were obtained. The values obtained in the NBS and D229 tests indicate that the poly(aryloxyphosphazenes) are superior to or competitive with current commercial plastics.

Dielectric properties (ASTM D149 and ASTM D150) of unhalogenated and halogenated poly(aryloxyphosphazenes) compared favorably with electrical grades of polyethylene and polyvinylchloride. Dielectric constants of about 3.3, dielectric

strengths of about 360 v/mil and power factors ranging from 0.001 to 0.040 over the frequency range 100 to 10^6 Hz were observed.

In general, the poly(aryloxyphosphazenes) showed good to excellent chemical resistance, particularly to dilute oxidants, dilute acids and strong alkalis. With the exception of $[(4\text{-BrC}_6\text{H}_4\text{O})_2\text{PN}]_n$, $[(2,4\text{-Cl}_2\text{C}_6\text{H}_3\text{O})_2\text{PN}]_n$ and $[(4\text{-ClC}_6\text{H}_4\text{O})_2\text{PN}-(2,4\text{-Cl}_2\text{C}_6\text{H}_3\text{O})_2\text{PN}]_n$ (1:3), all poly(aryloxyphosphazenes) were soluble in tetrahydrofuran and all alkylated poly(aryloxyphosphazenes) were soluble in chloroform.

TABLE OF CONTENTS

<u>Section</u>		<u>Page</u>
	Abstract	
1.0	Introduction and Summary	1
2.0	Experimental	5
2.1	Preparation and Characterization of Poly(aryloxyphosphazene) Homopolymers	6
2.1.1	$[(C_6H_5O)_2PN]_n$	6
2.1.2	$[(4-ClC_6H_4O)_2PN]_n$	6
2.1.3	$[(3-ClC_6H_4O)_2PN]_n$	11
2.1.4	$[(4-CH_3C_6H_4O)_2PN]_n$	11
2.1.5	$[(3-CH_3C_6H_4O)_2PN]_n$	11
2.1.6	$[(4-BrC_6H_4O)_2PN]_n$	11
2.1.7	$[(4-Cl-3-CH_3C_6H_3O)_2PN]_n$	14
2.2	Attempted Preparation of Poly(2-substituted aryloxyphosphazene) Homopolymers	14
2.2.1	$[(2,4-Cl_2C_6H_3O)_2PN]_n$	14
2.2.2	$[(2-ClC_6H_4O)_2PN]_n$	15
2.2.3	$[(2-CH_3C_6H_4O)_2PN]_n$	15
2.3	Preparation and Characterization of Poly(aryloxyphosphazene) Copolymers	15
2.3.1	$[(4-ClC_6H_4O)_2PN-(2,4-Cl_2C_6H_3O)_2PN]_n$	15
2.3.2	$[(C_6H_5O)_2PN-(2,4-Cl_2C_6H_3O)_2PN]_n$	16
2.3.3	$[(C_6H_5O)_2PN-(4-C_2H_5C_6H_4O)_2PN]_n$	16
2.3.4	$[(3-CH_3C_6H_4O)_2PN-(4-CH_3C_6H_4O)_2PN]_n$ (3:2)	23
2.4	Poly(aryloxyphosphazenes) Specimen Preparation	23

TABLE OF CONTENTS (continued)

<u>Section</u>		<u>Page</u>
3.0	Evaluation of Flame-Retardant and Electrical Properties	24
3.1	Limiting Oxygen Index (LOI)	24
3.2	National Electrical Manufacturers Test	24
3.3	National Bureau of Standards Smoke Density Chamber Test (Flaming)	24
3.4	Electrical Properties for the Poly(aryloxyphosphazenes)	24
4.0	Materials Supplied for Evaluation	29
5.0	Discussion	30
	References	39

LIST OF TABLES

<u>Number</u>		<u>Page</u>
I	Characterization of $[(RC_6H_4O)_2PN]_n$ Homopolymers	7
II	Preparation of $[(RC_6H_4O)_2PN]_n$ Homopolymers	9
III	Solvent and Chemical Resistance (ASTM D543) of Poly(aryloxyphosphazene) Homopolymers	12
IV	Characterization of $[(R_1C_6H_4O)_2PN-(R_2C_6H_4O)_2PN]_n$	17
V	Preparation of $[(R_1C_6H_4O)_2PN-(R_2C_6H_4O)_2PN]_n$ Copolymers	18
VI	Solvent and Chemical Resistance (ASTM D543) of Poly(aryloxyphosphazene) Copolymers	21
VII	Limiting Oxygen Index of $[(R_1C_6H_4O)_2PN-(R_2C_6H_4O)_2PN]_n$	25
VIII	Results of ASTM D229 (Method 2) for $[(RC_6H_4O)_2PN]_n$ Homopolymers	26
IX	NBS Smoke Test (Flaming) Results for $[(RC_6H_4O)_2PN]_n$ Homopolymers	27
X	Results of Electrical Tests for $[(RC_6H_4O)_2PN]_n$ Homopolymers	28
XI	Poly(aryloxyphosphazenes) Supplied for Evaluation	29
XII	Limiting Oxygen Index of Commercial Plastics	34
XIII	Comparison of Various Polymers According to ASTM D229	35
XIV	NBS Smoke Density Values for Polymers	36
XV	Comparison of Electrical Properties of Several Plastics	38

"SYNTHESIS OF PHOSPHONITRILIC PLASTICS AND ELASTOMERS FOR MARINE APPLICATIONS"

1.0 INTRODUCTION AND SUMMARY

In 1970 nearly 10.4 billion dollars in property losses and 12,200 deaths resulted because of fires [Ref. 1]. Particularly on-board ship, fires can exact a very costly toll in both life and property. An effort to develop new materials which were considerably more flame-resistant and less prone to generation of smoke and toxic fumes than existing materials was undertaken at Horizons Incorporated. This program was conducted from July 5, 1971 to November 4, 1972 under the sponsorship of the Army Materials and Mechanics Research Center (Contract DAAG-46-71-C-0103 P00003) with funds supplied by the Naval Ships Systems Command (NAVSEC).

The objective of the program was to prepare a family of inexpensive, flame-retardant polyphosphazene plastics and elastomers for use in various marine applications. Homopolymers and copolymers which contained (substituted) aryloxy substituents were selected as the most viable derivatives consistent with program goals. Indeed, the poly(aryloxyphosphazenes) which were prepared met or exceeded most of the property requirements which were specified for these new materials. These successes were even more dramatic because considerable effort was expended on development of proper procedures for synthesis and on preparation of large quantities of material for evaluation.

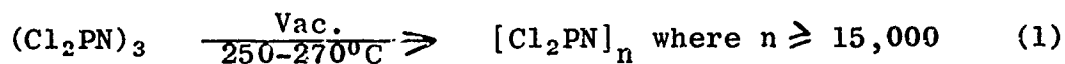
The rapid progress achieved in this program was due in part to prior expertise in the polyphosphazene field. Previously, Horizons Inc. had developed the poly(fluoroalkoxyphosphazenes) as extreme service, petroleum resistant elastomers [Ref. 2, 3]. These polymers have outstanding hydrolytic and chemical stability, are nonflammable, have low glass transition temperatures and good thermal stability and can be cured to develop good physical properties. However, the relatively high cost of these polymers precluded their use in large volume applications, and the less expensive poly(aryloxyphosphazenes) were found ideal for utilization as flame-retardant plastics and elastomers.

Monomeric nonfluorinated phosphazene compounds have been used in a variety of flame-retardant applications [Ref. 4]. The phosphazenes have great utility as flame retardants because of (1) the high percentage of phosphorus

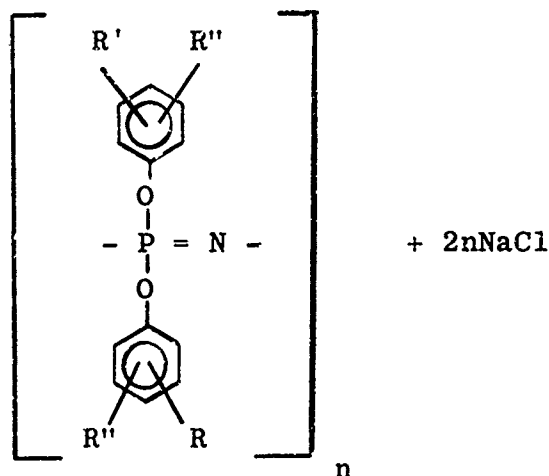
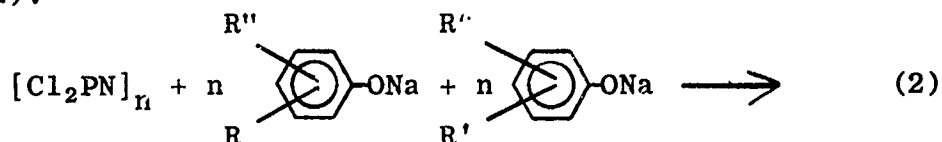
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present, (2) the simultaneous presence of large amounts of nitrogen in the molecule, and (3) the possibility of incorporation of halogen at the same time [Ref. 5].

The poly(aryloxyphosphazenes) were synthesized from soluble poly(dichlorophosphazene) which was prepared by the thermal ring opening of hexachlorophosphazene as shown in Equation (1).



Poly(dichlorophosphazene) in solution was reacted with a solution of the sodium salt(s) of the alcohol(s) to form fully substituted homopolymer or copolymer as shown in Equation (2).



where R, R' and R'' are selected from H, CH₃, C₂H₅, Cl, and Br

Eleven distinct and different polymers were prepared and characterized during the course of this program. These materials were prepared in an effort to define the influence of structure on physical properties and flame retardancy. Some preparations were carried out on a scale which gave kilogram quantities of product and other preparations were more modest in scale. The techniques employed in synthesis and purification are readily adaptable to commercialization.

Characterization of the homopolymers and copolymers routinely included intrinsic viscosity, elemental analyses, H^1 nuclear magnetic resonance spectra (for copolymers) solvent and chemical resistance, and Limiting Oxygen Index (LOI). Further evaluations of the various polymers were dependent on interest in the properties of the particular material and quantity of material available.

Homopolymers of the type $[(RC_6H_4O)_2PN]_n$ where $R = H$, $3-CH_3$, $4-CH_3$, $3-Cl$ and $4-Cl$ were prepared. A $[(4-ClC_6H_4O)_2PN-(2,4-Cl_2C_6H_3O)_2PN]_n$ copolymer also was prepared. These materials were plastics and formed strong, flexible films which oriented upon drawing. Other polymers prepared included $[(4-Cl-3-CH_3C_6H_3O)_2PN]_n$, $[(C_6H_5O)_2PN-(2,4-Cl_2C_6H_3O)_2PN]_n$ and $[(3-CH_3C_6H_4O)_2PN-(4-CH_3C_6H_4O)_2PN]_n$ (3:2) which were soft plastics. The $[(C_6H_5O)_2PN-(4-C_2H_5C_6H_4O)_2PN]_n$ copolymer was the sole elastomer prepared. Other poly(aryloxyphosphazene) elastomers are capable of preparation but they are less flame retardant and generally are more expensive than this derivative.

The anticipated high degree of flame retardancy for poly(aryloxyphosphazenes) was borne out for the above materials as unfilled and uncured specimens. Films of these polymers were self-extinguishing upon removal from a gas/oxygen flame, and many of these materials formed an intumescent char upon combustion. Furthermore, most of these polymers showed little tendency to drip during combustion.

All the poly(aryloxyphosphazenes) which were tested gave such outstanding values for the Hooker Laboratory Intermittent Test (HLT-15) [Ref. 6] that the test was abandoned in favor of tests which were more sensitive to polymer composition. Values for Limiting Oxygen Index (LOI, ASTM D2863) varied from 27 to 33 for nonhalogenated polymers and from 38 to 65 for halogenated derivatives. By comparison, current commercially available polymers are designated fire retardant (FR) if they have a LOI of 27 or greater. Results of the National Electrical Manufacturers Test (ASTM D229) were encouraging for the three homopolymers, $[(3-CH_3C_6H_4O)_2PN]_n$,

$[(C_6H_5O)_2PN]_n$ and $[(4-ClC_6H_4O)_2PN]_n$, which were studied. Ignition times (T_i) varied from 83 to 136 seconds whereas burn times (T_b) varied from 51 to 4.5 seconds, respectively. The $[(4-ClC_6H_4O)_2PN]_n$ homopolymer was outstanding with values of T_i and T_b of 136 and 4.5 seconds, respectively.

The high flame retardancy observed for the poly(aryloxyphosphazenes) only reflects one aspect of their outstanding flame-retardant performance. Generation of smoke with attendant loss of visibility and formation of toxic products during combustion are the primary cause of loss of life in a fire. Results of the National Bureau of Standards Smoke Density Test for the $[(4-CH_3C_6H_4O)_2PN]_n$, $[(C_6H_5O)_2PN]_n$ and $[(4-ClC_6H_4O)_2PN]_n$ homopolymers were very good ($D_{max}=261$), good (343) and fair (455), respectively. These values compare very favorably with many materials. For example, polystyrene, FR-acrylic and unfilled rigid polyvinyl chloride have values of D_{max} ranging from 470 to 535 [Ref. 7]. Samples were submitted to the sponsor for evaluation of toxicity of combustion products, but the results are not yet available.

Preliminary electrical properties (ASTM D149 and D150) were extremely encouraging for the only materials studied, i.e., the $[(C_6H_5O)_2PN]_n$, $[(3-CH_3C_6H_4O)_2PN]_n$, and $[(4-ClC_6H_4O)_2PN]_n$ homopolymers. Average dielectric strengths of 337-387 volts/mil were observed. Dielectric constants over the frequency range 100 to 10^6 Hz were 3.0 to 3.6. The power factor over this same frequency in no instance was greater than 0.040 ($[(3-CH_3C_6H_4O)_2PN]_n$) and was as low as 0.001 ($[(4-ClC_6H_4O)_2PN]_n$). For each homopolymer, moderately good stability of power factor was observed over the frequency range 100 to 10^6 Hz.

These values were obtained even though no effort was made to lower the (known) wide polydispersity of the samples or to develop fabrication techniques designed to optimize material properties for electrical applications. Efforts in either area would give improved electrical properties. Even so, the present values are comparable to electrical grade polyethylene or polyvinyl chloride.

Varying the nature of the substituent on the aryloxy ring affected not only flame-retardancy but also solubility. The $[(C_6H_5O)_2PN]_n$ and $[(4-ClC_6H_4O)_2PN]_n$ homopolymers and the $[(4-ClC_6H_4O)_2PN-(2,4-Cl_2C_6H_3O)_2PN]_n$ copolymer were soluble in tetrahydrofuran, swollen or soluble in chloroform, swollen by benzene and insoluble in ASTM fuels A, B and C. Alkylated (CH_3 , C_2H_5) poly(aryloxyphosphazene) homopolymers or copolymers were decidedly more soluble than the unsubstituted or halogenated counterparts. The $[(4-CH_3C_6H_4O)_2PN]_n$ homopolymer and

the $[(3\text{-CH}_3\text{C}_6\text{H}_4\text{O})_2\text{PN}-(4\text{-CH}_3\text{C}_6\text{H}_4\text{O})_2\text{PN}]_n$ (3:2), and $[(\text{C}_6\text{H}_5\text{O})_2\text{PN}-(4\text{-C}_2\text{H}_5\text{C}_6\text{H}_4\text{O})_2\text{PN}]_n$ copolymers were soluble in tetrahydrofuran, chloroform and benzene, and insoluble in ASTM fuel A. The two alkylated copolymers were swollen by ASTM fuel B and were soluble in ASTM fuel C, but $[(3\text{-CH}_3\text{C}_6\text{H}_4\text{O})_2\text{PN}]_n$ was insoluble in ASTM fuel B and swollen by ASTM fuel C.

During the course of this program, a variety of problems were addressed successfully. Commercially viable techniques for synthesis and purification were developed. Preliminary attempts towards certain types of fabrication of a few compounds were carried out.

Procedures were evolved for the preparation of a number of poly(aryloxyphosphazene) homopolymers and copolymers. Complete reaction of all phosphorus-chlorine bonds was achieved by manipulation of reaction solvent, temperature and time. Although completely substituted homopolymers could not be prepared which contained a substituent in the 2- position on the aryloxy- ring, copolymers which did contain a 2-substituent were prepared by sequential addition of the aryloxides. The poly(aryloxyphosphazenes) were purified by slurry extraction.

A reticulated foam of the $[(4\text{-ClC}_6\text{H}_4\text{O})_2\text{PN}]_n$ homopolymer was prepared by rapid evaporation of solvent from a Na_2SO_4 /polymer slurry and subsequent water leach. The $[(\text{C}_6\text{H}_5\text{O})_2\text{PN}-(4\text{-C}_2\text{H}_5\text{C}_6\text{H}_4\text{O})_2\text{PN}]_n$ elastomer was successfully compounded and cured with conventional fillers and peroxides.

Various poly(aryloxyphosphazene) homopolymers and copolymers were supplied to NAVSEC for further evaluation. The polymers will be evaluated by various Navy laboratories as foams and/or adhesives, and the products of combustion will be examined in order to determine smoke and toxicity.

Five gram samples of these materials were supplied to AMMRC for characterization. Their studies will include determination of number average and weight average molecular weights.

2.0 EXPERIMENTAL

Hexachlorophosphazene (El Monte Chemical Co.) was distilled rapidly at $120\text{-}128^\circ\text{C}/10\text{ mm}$. This material was sealed in evacuated pyrex tubes and was polymerized at 250° and 270°C for 6 to 30 hours and 4 to 16 hours, respectively. All phenols were obtained in at least 97% purity and were distilled or recrystallized before use. Solvents for the reactants were chosen so as to attain desired reaction temperatures and at the same time achieve some solubility of the product in the reaction mixture.

2.1 Preparation and Characterization of Poly(aryloxyphosphazene) Homopolymers

2.1.1 $[(C_6H_5O)_2PN]_n$

The $[Cl_2PN]_n$ polymer (900 g., 15.6 equivs.) was dissolved in 6.0 liters of dry benzene/chlorobenzene (7v/5v) and added in 5-1/2 hours to a dried (benzene azeotrope) solution (125°C) of sodium phenoxide which was prepared from phenol (2115 g., 22.5 moles) and sodium (476 g., 20.7 moles) in 12.0 liters of bis(2-methoxyethyl)ether (diglyme). The bis(2-methoxyethyl)ether which was obtained in 99+% purity from Ansul Company was heated with sodium and was distilled (b.p. 162-163°C) at atmospheric pressure. The reaction mixture was heated 23 hours at 125°C and 89 hours at 90°C. Polymer was precipitated by addition to 20.0 liters of methanol and was purified by washing with 20.0 liters of methanol, exhaustively washing with distilled water and was slurried twice with 10.0 liter portions of methanol. The product (993 g., 55.4% yield) was a white, fibrous solid. Flexible, moderately strong films which oriented upon drawing generally were prepared. Film properties were perhaps variable because of limited solubility (chloroform, tetrahydrofuran) at room temperature and/or because of differences in the polymers themselves. Intrinsic viscosity and elemental analysis are presented in Table I and experimental conditions and yields in Table II. Solvent and chemical resistance are shown in Table III.

2.1.2 $[(4-ClC_6H_4O)_2PN]_n$

The procedure outlined in Section 2.1.1 was followed. Quantities of reactants and solvents, and reaction conditions are presented in Table II. The solvent (9.25 liters) employed for the sodium 4-chlorophenoxide was bis(2-ethoxyethyl)ether-dioxane (3v/1v). Bis(2-ethoxyethyl)ether was purified by prolonged treatment with sodium followed by fractional distillation under vacuum. A large forerun was discarded before the main fraction was retained. The product (1076 g., 71% yield) obtained after exhaustive washing with methanol-water (1v/1v) was a finely divided powder. Films cast from tetrahydrofuran were generally opaque, flexible, tough, and oriented upon drawing. Intrinsic viscosity and elemental analysis are presented in Table I and solvent and chemical resistance is shown in Table III. Another preparation of this polymer was conducted which employed purified bis(2-methoxyethyl)ether and the resulting product also had good analysis (see Table II). The \bar{M}_n and \bar{M}_w were determined by AMMRC (Dr. Gary Hagnauer), for sample 1863-08, and found to be 2.2×10^5 and 2.1×10^6 , respectively.

TABLE I
CHARACTERIZATION OF $[(RC_6H_4O)_2PN]_n$ HOMOPOLYMERS*

Polymer R=	Sample No.	Intrinsic viscosity (30°C)		Analysis (%) ^a				T_g (°C)
		dl./g.	solvent	C	H	N	Cl	
H	1762-19	1.1 ^b	CHCl ₃	61.5 (62.3)	4.3 (4.3)	5.8 (6.1)	0.1 (0.0)	---
H	1980-20	1.5	THF	62.3 (62.3)	4.4 (4.3)	6.0 (6.1)	<1ppm (0.0)	---
4-Cl	1739-32	1.8 ^b	THF	48.2 (48.0)	2.8 (2.7)	---	23.3 (23.7)	- 3
4-Cl	1810-23	2.6	THF	50.2 (48.0)	2.9 (2.7)	3.7 (4.7)	21.1 (23.7)	+ 3.5
4-Cl	1810-43	2.3	THF	48.1 (48.0)	2.8 (2.7)	4.4 (4.7)	23.5 (23.7)	+ 5
4-Cl	1863-08	1.4	THF	48.0 (48.0)	2.7 (2.7)	4.7 (4.7)	23.6 (23.7)	---
3-Cl	1869-09	1.8	THF	48.0 (48.0)	2.9 (2.7)	4.7 (4.7)	23.6 (23.7)	-28
2-Cl ^c	1810-39 ^c	1.4	THF	46.1 (48.0)	2.8 (2.7)	---	24.3 (23.7)	---
4-CH ₃	1739-36	1.4 ^b	Ph	64.8 (64.8)	5.6 (5.4)	5.5 (5.4)	<100ppm (0.0)	- 3

(continued)

Table I (continued)

Polymer R=	Sample No.	Intrinsic Viscosity (30°C)		Analysis (%) ^a				T _g (°C)
		dl./g.	solvent	C	H	N	Cl	
4-CH ₃	1863-01	2.1	Ph	65.0 (64.8)	5.4 (5.4)	5.0 (5.4)	0.01 (0.0)	0
3-CH ₃	1847-30	2.1	Ph	64.6 (64.8)	5.5 (5.4)	5.6 (5.4)	0.2 (0.0)	---
3-CH ₃	1810-01	1.8 ^b	Ph	64.6 (64.8)	5.6 (5.4)	5.2 (5.4)	0.1 (0.0)	-27
2-CH ₃ ^c	1810-36 ^c	1.0	Ph	62.3 (64.8)	5.1 (5.4)	5.5 (5.4)	3.9 (0.0)	---
4-Br ^c	1863-16 ^c	1.0	THF	39.0 (37.0)	2.3 (2.1)	3.4 (3.6)	0.035 ^d (0.0)	---
4-Br	1911-21	---	CHCl ₃	37.0 (37.0)	1.8 (2.1)	3.6 (3.6)	0.01 ^e (0.0)	---
2,4-Cl ₂ ^c	1762-38 ^c	---	---	39.4 (39.1)	1.7 (1.6)	---	36.4 (38.4)	---
4-Cl-3-CH ₃	1762-11	1.4 ^b	Ph	50.6 (51.1)	3.8 (3.9)	4.3 (4.3)	20.9 (21.6)	-17

Legend

Ph benzene
 THF tetrahydrofuran
 DMF N,N-dimethylformamide

*-All materials were plastics

a-Calculated values in parentheses

b-28°C

c-Known anomalous substitution or crosslinked

d-Br, 37.0 (41.1)

e-Br, 41.2 (41.1)

TABLE II

PREPARATION OF $[(RC_6H_4O)_2PN]_n$ HOMOPOLYMERS

Polymer (R) Sample No.	[Cl ₂ PN] ⁿ Reactant		Aryloxy Reactant			Reaction Conditions		Product Yield	
	g. equivs.	solvent v/v ratio	Phenol g. moles	Sodium		Temp. (°C)	Time (hrs)	%	g.
				g. moles	solvent v/v ratio				
H 1762-19	11.8 0.20	Ph/T 1:1	22.7 0.24	5.3 0.23	C/DI 3:1	115	43	33 ^a	7.8
H 1880-20	900 15.6	Ph/CB 7:5	2115 22.5	476 20.7	DG	125 90	23 89	55	993
4-Cl 1739-32	50.0 0.86	Ph/T 3:2	133 1.04	21.3 0.93	C/DI 3:1	124-7	25	54 ^a	70
4-Cl 1810-23	345 6.0	Ph	1543 12.0	253 11.0	DC/DI 3:1	128	24	85 ^a	763
4-Cl 1810-43	22.1 0.38	CB	30.4 0.24	5.1 0.22	DC/DI 3:1	125	36	70 ^a	29
4-Cl 1863-08	583 10.10	Ph/CB 7:5	1620 12.6	269 11.6	DC/DI 3:1	125	22.5	71	1076
3-Cl 1869-09	60 1.04	Ph	167 1.30	27.9 1.20	C/DI 3:1	125	32	28 ^a	44
2-Cl 1810-39	79.0 1.36	Ph/CB 4:5	219.0 1.70	37.0 1.61	C/DI 3:1	135	19	43 ^a	87
4-CH ₃ 1739-36	194 3.34	Ph/X 5:3	435 4.02	85 3.70	C/DI 3:1	115 125-7	8 34	53 ^b	239
4-CH ₃ 1863-01	100 1.72	Ph/X 1:1	246 2.28	45.5 1.98	C/DI 3:1	125	36	64	143

TABLE II (continued)

Polymer (R) Sample No.	[Cl ₂ PN] _n Reactant	Sodium Aryloxyde Reactant		Reaction Conditions		Product Yield	
		Phenol g. moles	Sodium g. moles	Temp. (°C)	Time (hrs)	%	g.
3-CH ₃ 1847-30	600 10.32	1476 12.54	273 11.9	124	78	68	908
3-CH ₃ 1810-01	112.2 1.94	250.1 2.32	48.9 2.13	126	28	51 ^b	127
2-CH ₃ 1810-36	50.0 0.86	121.3 1.13	22.8 1.0	128	19	52 ^{b+c}	58
4-Br 1863-16	75.5 1.30	288 1.67	38.0 1.65	132	30	63	162
4-Br 1911-21	85.8 1.48	320 1.85	92 ^d 1.70	127	50	90	251
2,4-Cl ₂ 1762-38	11.6 0.20	40.7 0.25	5.3 0.23	147	27	100	39
4-Cl-3-CH ₃ 1762-11	130.8 2.26	356.5 2.5	54.6 2.38	93	52	50	187

Legend

Ph-Benzene	C-Bis(2-ethoxyethyl)ether
T- Toluene	DC-C distilled from Na
CB-Chlorobenzene	DI-Dioxane
X-Xylene	DG-Bis(2-methoxyethyl)ether

- a by H₂O/CH₃OH washing, dissolving in THF, and precipitating into CH₃OH.
 b by dissolving in chlorinated hydrocarbon, H₂O washing and precipitating into CH₃OH.
 c by dissolving in C₆H₆, H₂O washing, and precipitating into CH₃OH.
 d sodium methoxide instead of sodium.

A reticulated foam was prepared with the $[(4-\text{ClC}_6\text{H}_4\text{O})_2\text{PN}]_n$ homopolymer (1810-23) by the formation of a $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$ (-14 to 200 mesh) slurry in tetrahydrofuran. Fyrquel 220 (Stauffer Chemical Co.) and Cab-O-Sil M-S (the Cabot Corp.) also were added to improve processing and final properties. Solvent was removed under vacuum and salt was removed by leaching with warm water. The foam showed some tendency to develop a smooth skin and was open-celled and quite flexible.

2.1.3 $[(3-\text{ClC}_6\text{H}_4\text{O})_2\text{PN}]_n$

The procedure described in Section 2.1.2 generally was followed. Quantities of reactants, solvents and reaction conditions employed and product yield are given in Table II. Characterization data of the product are given in Table I and solvent and chemical resistance are given in Table III. Films cast from tetrahydrofuran were flexible and showed moderate strength and orientation upon drawing.

2.1.4 $[(4-\text{CH}_3\text{C}_6\text{H}_4\text{O})_2\text{PN}]_n$

The procedures described in Sections 2.1.1 and 2.1.2 generally were followed. Quantities of reactants, solvents and reaction conditions employed and product yield are given in Table II. Characterization data of the product are given in Table I and solvent and chemical resistance are given in Table III. Films of this polymer cast from benzene were flexible, moderately strong, and showed a moderate degree of orientation upon drawing.

2.1.5 $[(3-\text{CH}_3\text{C}_6\text{H}_4\text{O})_2\text{PN}]_n$

The procedure described in Section 2.1.1 was essentially followed. Quantities of reactants, solvents and reaction conditions employed and product yield are given in Table II. Characterization data of the product are given in Table I and solvent and chemical resistance are given in Table III. Films of this polymer cast from benzene were very flexible, strong and showed considerable orientation upon drawing.

2.1.6 $[(4-\text{BrC}_6\text{H}_4\text{O})_2\text{PN}]_n$

The $[\text{Cl}_2\text{PN}]_n$ polymer mixture (85.8 g., 1.48 equivs.) was dissolved in 650 ml. benzene and added over 30 minutes to a dried (benzene azeotrope) solution at 125°C of sodium

TABLE III

SOLVENT AND CHEMICAL RESISTANCE (ASTM D543)
OF POLY(ARYLOXYPHOSHAZENE) HOMOPOLYMERS

	$[(C_6H_5O)_2PN]_n$		$[(4-ClC_6H_4O)_2PN]_n$		$[(3-ClC_6H_4O)_2PN]_n$		$[(4-CH_3C_6H_4O)_2PN]_n$		$[(3-CH_3C_6H_4O)_2PN]_n$		$[(4-BrC_6H_4O)_2PN]_n$		$[(4-Cl-3-CH_3C_6H_4O)_2PN]_n$	
Acetone	S	SW	I		I		I		I		I		I	
Aniline	S	SW	I		-		SW		SW		-		-	
Benzene	S	SW	I		SW		S		SW		S	SW	S	
Carbon tetra- chloride		I	S	SW	-		SW		SW		-		-	
Chloroform		I	S	SW	S		S		S		I		S	
Diethyl ether		I	S	SW	-		I		I		-		-	
Di-2-ethylhexyl sebacate		I		I	-		I		I		-		-	
N,N-dimethylformamide	SW		S	SW	I		I		I		I		I	
Ethyl acetate	SW		S	SW	I		I		I		I		S	SW
Ethanol (95%)		I		I	I		I		I		I		I	
Ethylene dichloride		I	S	SW	-		S	SW	S	SW	-		-	
Methanol		I		I	-		I		I		-		-	
Methyl heptafluoro- butyrate		I		I	-		I		I		-		-	
Olive oil		I		I	-		I		I		-		-	
Pyridine	SW		S	SW	-		SW		S	SW	-		-	
Tetrahydrofuran		S		S	S		S		SW		S	SW	S	
ASTM Fuel A (isooctane)		I		I	I		I		I		I		I	

(continued)

TABLE III (continued)

	$[(C_6H_5O)_2PN]_n$	$[(4-ClC_6H_4O)_2PN]_n$	$[(3-ClC_6H_4O)_2PN]_n$	$[(4-CH_3C_6H_4O)_2PN]_n$	$[(3-CH_3C_6H_4O)_2PN]_n$	$[(4-BrC_6H_4O)_2PN]_n$	$[(4-Cl-3-CH_3C_6H_4O)_2PN]_n$
ASTM Fuel B (isooctane-toluene, 70v/30v)	I	I	I	I	I	I	SW
ASTM Fuel C (isooctane-toluene, 50v/50v)	S SW	I	I	I	I	I	S
Acetic acid (glacial)	I	I	-	I	I	-	-
Ammonium hydroxide (conc.)	I	I	-	I	I	-	-
Chromic acid (40%)	I	I	I	I	I	I	I
				(chars)			
Hydrochloric acid (conc.)	I	I	-	I	I	-	-
Hydrofluoric acid (40%)	I	I	I	I	I	I	I
Hydrogen peroxide (28%)	I	I	-	I	I	-	-
Nitric acid (70%)	I	I	I	S SW	-	I	S SW
Sodium chloride (10%)	I	I	-	I	I	-	-
Sodium hydroxide (60%)	I	I	-	I	I	-	-
Sodium hypochlorite (4-6%)	I	I	-	I	I	-	-
Sulfuric acid (conc.)	S	I	I	SW	I	S SW	I
Sulfuric acid (30%)	I	I	I	I	I	I	I

Legend

S - Soluble
SW - Swells

S SW - Slight Swelling
I - Insoluble

4-bromophenoxide which was prepared from 4-bromophenol (320 g., 1.85 moles) and sodium methoxide (92 g., 1.70 moles) in 1.2 liters of bis(2-methoxyethyl)ether. The resulting methanol was removed by addition of benzene followed by azeotropic distillation until gas chromatography revealed no methanol in the distillate. Reaction conditions and yields are given in Table II and characterization data in Table I. The homopolymer softened at 90-140°C and underwent melting at 180-190°C. Solvent and chemical resistance are shown in Table III. This polymer was almost completely soluble in hot ($\geq 100^\circ\text{C}$) chlorobenzene.

The new procedure for the preparation of the aryloxy was necessary because an earlier preparation conducted in the normal manner apparently led to formation of a small but unspecified amount of sodium phenoxide probably by reductive cleavage of the carbon bromine bond. This side reaction was suspected when the product was examined by Proton NMR, solubility, and elemental analysis and was believed to be a copolymer. For example, the polymer obtained when sodium methoxide was used was insoluble in all common solvents at room temperature. On the other hand, the polymer obtained when sodium metal was used was quite soluble in tetrahydrofuran. This type of side reaction also could occur in the preparation of chlorophenoxides, although the rate would be much lower. This possibility was not investigated during this program.

2.1.7 $[(4\text{-Cl-3-CH}_3\text{C}_6\text{H}_3\text{O})_2\text{PN}]_n$

The procedure described in Section 2.1.1 essentially was followed except that the product was purified by solution in 2.5 liters of chlorobenzene-benzene (4v/1v) followed by a water wash and a precipitation by addition to methanol. Quantities of reactants, solvents and reaction conditions employed and product yield are given in Table II. Characterization data is given in Table I and solvent and chemical resistance are given in Table III. Films cast from benzene were soft and very flexible.

2.2 Attempted Preparation of Poly(2-substituted aryloxy-phosphazene) Homopolymers

2.2.1 $[(2,4\text{-Cl}_2\text{C}_6\text{H}_3\text{O})_2\text{PN}]_n$

The $[\text{Cl}_2\text{PN}]_n$ polymer (11.6 g., 0.20 equiv.) was dissolved in 170 ml. of dry benzene and added over 20 minutes to a predried (benzene azeotrope) solution of sodium 2,4-dichlorophenoxide which was prepared from 2,4-dichlorophenol (40.7 g., 0.25 mole) and sodium (5.3 g., 0.23 mole) in 150 ml. bis(2-methoxyethyl)ether. Additional solvent (chlorobenzene, 225 ml.) was added to the mixture which was heated for 27

hours at 147°C. Polymer was precipitated by addition of 1 liter of methanol and was washed exhaustively with methanol-water. The product (39.3 g., 100% yield) was an extremely fine white powder which was insoluble in all common solvents and softened at 255-270°C. Anal. Calcd. for $[(Cl_2C_6H_3O)_2PN]_n$: C, 39.1; H, 1.6; Cl, 38.4. Found: C, 39.4; H, 1.7; Cl, 36.4.

Extraction of the product with warm N,N-dimethylformamide (DMF) afforded about 10% of lower softening (190°C) powder with an intrinsic viscosity in DMF of 0.02 dl./g. at 28°C. The elemental analysis of this soluble material was essentially identical to that of the original material.

A second experiment was conducted at 123°C (46 hours) and afforded product with essentially identical melting behavior, solubility and elemental analysis.

2.2.2 $[(2-ClC_6H_4O)_2PN]_n$

The procedure described in Section 2.1.2 generally was followed. Quantities of reactants, solvents and reaction conditions employed and product yield are given in Table II. Anal. Calcd. for $[(ClC_6H_4O)_2PN]_n$: C, 48.0; H, 2.7; Cl, 23.7. Found: C, 46.1; H, 2.8; Cl, 24.3. This material was soluble in chloroform and benzene and slightly swollen by acetone and ASTM fuels A, B, and C.

2.2.3 $[(2-CH_3C_6H_4O)_2PN]_n$

The procedure described in Section 2.2.1 generally was followed. Quantities of reactants, solvents and reaction conditions employed and product yield are given in Table II. Anal. Calcd. for $[(2-CH_3C_6H_4O)_2PN]_n$: C, 64.8; H, 5.4; N, 5.4; Cl, 0.0. Found: C, 62.3; H, 5.1; N, 5.5; Cl, 3.9. Because of the high chlorine content this material was not further characterized.

2.3 Preparation and Characterization of Poly(aryloxyphosphazene) Copolymers (1:1 mole ratio)

2.3.1 $[(4-ClC_6H_4O)_2PN-(2,4-Cl_2C_6H_3O)_2PN]_n$

Sodium 2,4-dichlorophenoxide was prepared from 2,4-dichlorophenol (225 g., 1.38 moles) and sodium (29.5 g., 1.30 moles) in 1 liter of purified bis(2-methoxyethyl)ether. Sodium 4-chlorophenoxide was prepared separately from 4-chlorophenol (177.7 g., 1.38 moles) and sodium (29.5 g., 1.30 moles) in 1 liter of purified bis(2-methoxyethyl)ether. In contrast

to the procedure of Section 2.1.1, the derivatization was conducted by addition of sodium 2,4-dichlorophenoxide to a solution of $[\text{Cl}_2\text{PN}]_n$ polymer (145 g., 2.52 equivs.) in 800 ml. of dry benzene-xylene (5v/3v) at ambient temperature with stirring. The mixture was warmed to 100°C , the sodium 4-chlorophenoxide was added and the temperature was raised to 130°C . The reaction mixture was maintained at 130°C for 31 hours. Polymer was precipitated by addition of 2 liters of methanol and was washed exhaustively with methanol-water (1v/1v). The solid was dissolved in 8 liters of tetrahydrofuran and precipitated into 20 liters of distilled water. The product (130 g., 31% yield) was a granular plastic which gave (tetrahydrofuran) flexible, moderately strong films, which showed moderate orientation upon drawing. Characterization data are given in Table IV and experimental conditions are summarized in Table V. Solvent and chemical resistance are shown in Table VI.

An attempted preparation of the title compound with a 1:3 mole ratio was unsuccessful. The procedure outlined above was followed except that pure bis(2-ethoxyethyl)ether-dioxane (3v/1v) was employed for the aryloxy salts. Table V gives the quantities of respective phenols and sodium which were employed. Sodium 4-chlorophenoxide was added at 130°C and the reaction completed by heating at 132°C . The product was isolated but the extreme insolubility and poor elemental analysis indicated the sample probably was crosslinked. Anal. Calcd. for $[(\text{ClC}_6\text{H}_4\text{O})_2\text{PN}-(\text{Cl}_2\text{C}_6\text{H}_3\text{O})_2\text{PN}]_n$ (1:3 mole ratio): C, 40.1; H, 1.9; N, 4.0; Cl, 35.3. Found: C, 40.5; H, 2.2; N, 3.7. Cl, 36.4.

2.3.2 $[(\text{C}_6\text{H}_5\text{O})_2\text{PN}-(2,4-\text{Cl}_2\text{C}_6\text{H}_3\text{O})_2\text{PN}]_n$

The procedure outlined in Section 2 3.1 generally was followed except that sodium phenoxide was substituted for sodium 4-chlorophenoxide. Quantities of reactants, solvents and reaction conditions employed and product yield are given in Table V. Characterization data are given in Table IV and solvent and chemical resistance are given in Table VI. Films cast from tetrahydrofuran were very flexible, slightly weak and showed moderate orientation upon drawing.

2.3.3 $[(\text{C}_6\text{H}_5\text{O})_2\text{PN}-(4-\text{C}_2\text{H}_5\text{C}_6\text{H}_4\text{O})_2\text{PN}]_n$

The procedure outlined in Section 2.1.1 was generally followed except that equimolar amounts of phenol and 4-ethylphenol were employed. Quantities of reactants,

TABLE IV

CHARACTERIZATION OF $[(R_1C_6H_4O)_2PN-(R_2C_6H_4O)_3PN]_n$ COPOLYMERS (1:1 mole ratio)

Polymer $R_1 =$	$R_2 =$	Sample No.	Phys. State	Intrinsic Viscosity (30°C) dl./g. Solvent	Analysis (%) ^a				Tg(°C)
					C	H	N	Cl	
H	4-C ₂ H ₅	1672-14	E	0.6 ^b	64.3 (64.9)	5.5 (5.4)	---	0.03 (0.0)	-27
H	4-C ₂ H ₅	1762-04	E	2.7 ^b	64.5 (64.9)	5.5 (5.4)	5.4 (5.4)	0.6 (0.0)	-16
H	4-C ₂ H ₅	1847-46	E	2.3	64.9 (64.9)	5.4 (5.4)	5.4 (5.4)	0.1 (0.0)	---
3-CH ₃ ^c	4-CH ₃ ^c	1739-22	P	1.6	61.2 (64.9)	5.0 (5.4)	5.3 (5.4)	2.2 (0.0)	-20
3-CH ₃ ^c	4-CH ₃ ^c	1962-10	P	1.5	64.2 (64.9)	5.2 (5.4)	5.4 (5.4)	0.1 (0.0)	---
H	2,4-Cl ₂	1869-42	P	1.4	47.8 (48.0)	2.8 (2.7)	4.8 (4.7)	24.5 (23.7)	---
4-Cl	2,4-Cl ₂	1681-26	P	2.3 ^b	42.8 (43.0)	2.5 (2.1)	---	31.8 (31.8)	+25
4-Cl	2,4-Cl ₂	1829-50	P	1.8	42.9 (43.0)	2.3 (2.1)	4.1 (4.2)	31.7 (31.8)	+21
4-Cl ^d	2,4-Cl ₂ ^d	1863-12	P	---	40.5 (40.1)	2.2 (1.9)	3.7 (4.0)	36.4 (35.3)	---

Legend

E-Elastomer

P-Plastic

Ph-Benzene

THF-Tetrahydrofuran

a-Calculated values in parentheses

b-28°C

c-3:2 mole ratio of R₁:R₂d-1:3 mole ratio of R₁:R₂

TABLE V

PREPARATION OF $[(R_1C_6H_4O)_2PN-(R_2C_6H_4O)_2PN]_n$ COPOLYMERS

Polymer $\frac{R_1}{(R_1:R_2)}$	Samp. No.	[Cl ₂ PN] _n Reactant		Sodium Aryloxyide(s) Reactant		Reaction Conditions Temp. Time (°C) (hrs.)	Prod. Yield %
		g. equivs.	solvent v/v ratio	$\frac{R_1 \& R_2}{\text{phenol}}$ g. moles	$\frac{\text{sodium}}{\text{g.}} \frac{\text{solvent}}{\text{v/v ratio}}$		
H 4-C ₂ H ₅ (1:1)	1672-14	104 1.80	T	88 H 0.95	C	80 20	47 110
						100 33	
						125-135 94	
H 4-C ₂ H ₅ (1:1)	1762-04	208 3.60	Ph	177.6 H 1.89	C/DI (1:1)	95 73	^b 31 183
H 4-C ₂ H ₅ (1:1)	1847-46	782 13.48	Ph	677.9 H 7.24	C/DG (3:13)	123 56	^b 31 547
3-CH ₃ 4-CH ₃ (3:2)	1739-22	128 2.20	Ph	160 3-CH ₃ 1.48	DI	93 44	^b 45 130
				4-C ₂ H ₅ 104 0.96			

(continued)

Table V (continued)

Polymer $\frac{R_1}{R_2}$ ($R_1:R_2$)	Samp. No.	[Cl ₂ PN]n Reactant		Sodium Aryloxyde(s) Reactant		Reaction Conditions Temp. Time (°C) (hrs.)	Prod. Yield %			
		g. equivs.	solvent v/v ratio	$R_1 \& R_2$ /phenol g. moles	sodium g. moles					
3-CH ₃ 4-CH ₃ (3:2)	1962-10	$\frac{839}{14.4}$	$\frac{Ph/CB}{3:2}$	3-CH ₃	$\frac{1172.8}{10.9}$	DG	123- 125	41	26	488
				4-CH ₃	$\frac{781.9}{7.2}$					
H 2,4-Cl ₂ (1:1)	1869-42	$\frac{138}{2.40}$	$\frac{Ph/CB}{5:3}$	H	$\frac{123.8}{1.32}$	DG	130	148	69	248
				2,4-Cl ₂	$\frac{208.0}{1.27}$					
4-Cl 2,4-Cl ₂ (1:1)	1681-26	$\frac{58}{1.00}$	T	4-Cl	$\frac{71.1}{0.55}$	C	110 125- 130	1 22	72 ^b	121
				2,4-Cl ₂	$\frac{90.2}{0.55}$					
4-Cl 2,4-Cl ₂ (1:1)	1829-50	$\frac{145}{2.52}$	$\frac{Ph/X}{2.1}$	4-Cl	$\frac{177.7}{1.38}$	DG	130	31	31 ^a	130
				2,4-Cl ₂	$\frac{225.0}{1.38}$					

(continued)

Table V (continued)

Polymer $\frac{R_1}{R_2}$ ($R_1:R_2$)	Samp. No.	[Cl ₂ PN] n		R ₁ &R ₂ /phenol		Sodium Aryloxyde(s) Reactant		Reaction Conditions		Prod. Yield
		g. equivs.	solvent v/v ratio	g. moles	g. moles	g. moles	solvent v/v ratio	Temp. (°C)	Time (hrs.)	% g.
4-Cl 2,4-Cl ₂ 1863-12 (1:3)		116 2.00	Ph	4-Cl 83.5 0.65	13.8 0.60	DC/DI (3:1)		130- 132	68	65 228
				2,4-Cl ₂ 269 1.65	30.5 1.55					

Legend

Ph-Benzene	C-Bis(2-ethoxyethyl)ether
T-Toluene	DC-C distilled from Na
CB-Chlorobenzene	DI-Dioxane
X-Xylene	DG-Bis(2-methoxyethyl)ether

a-by H₂O/CH₃OH washing, dissolving in THF, and precipitating into CH₃OH
b-by dissolving in chlorinated hydrocarbon, H₂O washing and precipitating into CH₃OH
c-by dissolving in C₆H₆, H₂O washing, and precipitating into CH₃OH

TABLE VI

SOLVENT AND CHEMICAL RESISTANCE (ASTM D543)
OF POLY(ARYLOXYPHOSPAZENE) COPOLYMERS

	$[(\text{C}_6\text{H}_5\text{O})_2\text{PN}-(2,4\text{-Cl}_2\text{C}_6\text{H}_3\text{O})_2\text{PN}]_n$	$[(4\text{-ClC}_6\text{H}_4\text{O})_2\text{PN}-(2,4\text{-Cl}_2\text{C}_6\text{H}_3\text{O})_2\text{PN}]_n$	$[(\text{C}_6\text{H}_5\text{O})_2\text{PN}-(4\text{-C}_2\text{H}_5\text{C}_6\text{H}_4\text{O})_2\text{PN}]_n$	$[(3\text{-CH}_3\text{C}_6\text{H}_4\text{O})_2\text{PN}-(4\text{-CH}_3\text{C}_6\text{H}_4\text{O})_2\text{PN}]_n$
Acetone	I	I	S SW	S
Aniline	S SW	I	S	SW
Benzene	S	I	S	S
Carbon tetrachloride	S	I	S	S
Chloroform	S	SW	S	S
Diethyl ether	S	I	S	S
Di-2-ethylhexyl sebacate	-	I	-	-
N,N-dimethylformamide	S	I	S	S
Ethyl acetate	S	I	S	S
Ethanol (95%)	I	I	S SW	I
Ethylene dichloride	S	I	S	S
Methanol	-	I	I	I
Methyl heptafluorobutyrate	-	I	I	I
Olive oil	-	I	I	I
Pyridine	S	S SW	S	S
Tetrahydrofuran	S	S	S	S
ASTM Fuel A (isooctane)	I	I	S SW	I
ASTM Fuel B (isooctane-toluene, 70v/30v)	I	I	S SW	S SW
ASTM Fuel C (isooctane-toluene, 50v/50v)	S SW	I	S	S
Acetic acid (glacial)	-	I	S SW	S SW

(continued)

TABLE VI (continued)

	$[(C_6H_5O)_2PN-(2,4-Cl_2C_6H_3O)_2PN]_n$	$[(4-ClC_6H_4O)_2PN-(2,4-Cl_2C_6H_3O)_2PN]_n$	$[(C_6H_5O)_2PN-(4-C_2H_5C_6H_4O)_2PN]_n$	$[(3-CH_3C_6H_4O)_2PN-(4-CH_3C_6H_4O)_2PN]_n$
Ammonium hydroxide (conc.)	-	I	I	I
Chromic acid (40%)	I	I	SW	I
Hydrochloric acid (conc.)	-	I	I	I
Hydrofluoric acid (40%)	I	I	S	S
Hydrogen peroxide (28%)	-	I	I	I
Nitric acid (70%)	I	I	SW	SW
Sodium chloride (10%)	-	I	I	I
Sodium hydroxide (60%)	-	I	I	I
Sodium hypochlorite (4-6%)	-	I	I	I
Sulfuric acid (conc.)	I	I	S SW	SW
Sulfuric acid (30%)	I	I	I	I

Legend

S - Soluble

SW - Swells

S SW - Slight Swelling

I - Insoluble

solvents and reaction conditions employed and product yield are given in Table V. Characterization data of the product are given in Table IV and solvent and chemical resistance is given in Table VI. The polymer was crosslinked by casting a 5-10% solution in benzene containing tert-butyl peroctoate (3% on polymer) and then heating 1 hour at 100°C. The vulcanizate was clear and was insoluble in benzene. Similar results could be obtained by conventional molding and pressing techniques in the presence of fillers and other peroxides.

2.3.4 $[(3-\text{CH}_3\text{C}_6\text{H}_4\text{O})_2\text{PN}-(4-\text{CH}_3\text{C}_6\text{H}_4\text{O})_2\text{PN}]_n$ (3:2)

The procedure outlined in Section 2.1.1 was followed generally except that a mixture of 3-methylphenol (60 mole %) and 4-methylphenol (40 mole %) was used instead of phenol. Quantities of reactants, solvents and reaction conditions employed and product yield are given in Table V. Characterization data of the product are given in Table IV and solvent and chemical resistance are given in Table VI. The films cast from benzene were very flexible, very extendable, and moderately weak.

2.4 Poly(aryloxyphosphazenes) Specimen Preparation

Specimens for various flammability and electrical tests were prepared as follows. Films of the poly(aryloxyphosphazene) plastics were obtained by slow evaporation at room temperature of 5-10% solutions in benzene or tetrahydrofuran with subsequent vacuum drying. Thin, flexible sheets of the $[(3-\text{CH}_3\text{C}_6\text{H}_4\text{O})_2\text{PN}]_n$ and $[(4-\text{CH}_3\text{C}_6\text{H}_4\text{O})_2\text{PN}]_n$ homopolymers and their copolymers (3:2) and the $[(\text{C}_6\text{H}_5\text{O})_2\text{PN}]_n$ homopolymer were prepared by compression molding. The $[(3-\text{CH}_3\text{C}_6\text{H}_4\text{O})_2\text{PN}]_n$ homopolymer was rolled on a warm (65°C) 2-roll rubber mill to give transparent sheets. A few other materials were less satisfactory on compression molding and this behavior may be due to molding conditions or to inherent properties of the polymer. No effort to optimize molding conditions was undertaken. Generally, molding was accomplished at relatively low temperatures and high pressures (~130°C, 6000 psi) in a short period (~5 minutes).

3.0 EVALUATION OF FLAME-RETARDANT AND ELECTRICAL PROPERTIES

3.1 Limiting Oxygen Index (LOI)

This test was conducted according to procedures given in ASTM D2863 on specimens (6" x 1/4" x 1/8") molded under pressure. The values of Limiting Oxygen Index obtained for poly(aryloxyphosphazene) homopolymers and copolymers are given in Table VII. Generally, one to three specimen bars were required to determine the prescribed burning rate. The calibration standard was Rohm and Haas Plexiglass UVA11 which gave a value of 18. During combustion several polymers formed a sizeable intumescent char; these were the $[(C_6H_5O)_2PN]_n$, $[(4-ClC_6H_4O)_2PN]_n$, $[(3-ClC_6H_4O)_2PN]_n$, $[(4-3rC_6H_4O)_2PN]_n$ homopolymers and the $[(4-ClC_6H_4O)_2PN-(2,4-Cl_2C_6H_3O)_2PN]_n$ copolymer.

3.2 National Electrical Manufacturers Test

The test methods (ASTM D229, Method 2) for rigid sheet and plate insulation were employed except a single sample of $[(C_6H_5O)_2PN]_n$ and three and two samples, respectively, each of the $[(4-ClC_6H_4O)_2PN]_n$ and $[(3-CH_3C_6H_4O)_2PN]_n$ homopolymers were tested. Samples (8" x 1/2" x 1/2") were prepared by compression molding and the ignition times (T_i) and burn times (T_b) which were obtained are given in Table VIII. For comparative purposes, the LOI ratings of these polymers also are given.

3.3 National Bureau of Standards Smoke Density Chamber Test (Flaming)

Films (3" x 3" x ≈ 0.02 ") were prepared by casting from solution. Benzene was used for $[(4-CH_3C_6H_4O)_2PN]_n$ and tetrahydrofuran was used for $[(C_6H_5O)_2PN]_n$ and $[(4-ClC_6H_4O)_2PN]_n$. The samples were dried to constant weight under high vacuum and conditioned 48 hours at 23°C and 50% relative humidity prior to testing. Two films of each polymer were tested and the results of maximum specific optical density (D_m), time to reach 90% D_m and the maximum rate are given in Table IX.

3.4 Electrical Properties for the Poly(aryloxyphosphazenes)

Samples of 4" x 4" x $\approx 1/8$ " were prepared by compression molding. The results of three samples per polymer and the average values are shown in Table X. The samples were tested at 74°C at 50% relative humidity. Oil was used as the test medium for ASTM D149.

TABLE VII

LIMITING OXYGEN INDEX OF $[(R_1C_6H_4O)_2PN-(R_2C_6H_4O)_2PN]_n$

Polymer		Mole Ratio of $R_1:R_2$	LOI
R_1	R_2		
H	H	-	33
4-Cl	4-Cl	-	43-44
3-Cl	3-Cl	-	51
4-CH ₃	4-CH ₃	-	27
3-CH ₃	3-CH ₃	-	28
4-Br	4-Br	-	65
{ 3-CH ₃ } { 4-Cl }	3-CH ₃ 4-Cl	-	38
H	2,4-Cl ₂	1:1	43
H	4-C ₂ H ₅	1:1	27-28 ^a
4-Cl	2,4-Cl ₂	1:1	59
3-CH ₃	4-CH ₃	≈ 3:2	27

^a uncorrected value; a thin nichrome wire placed in center of sample to render it more rigid

TABLE VIII
RESULTS OF ASTM D229 (METHOD 2) FOR $[(RC_6H_4O)_2PN]_n$ HOMOPOLYMERS

<u>Polymer R =</u>	<u>Sample No.</u>	<u>Ignition Time (sec.)</u>	<u>Burn Time (sec.)</u>	<u>LOI</u>
H	1880-06	115	51	33
4-Cl	1863-30	121 151	3 6	43-44
4-Cl	1739-31	121	3	43-44
3-CH ₃	1847-30	82 83	73 31	28

TABLE IX

NBS SMOKE TEST (FLAMING) RESULTS FOR $[(RC_6H_4O)_2PN]_n$ HOMOPOLYMERS

Polymer R=	Film		D_{max}	Max. Rate (min.)	Time to Reach 90% D_{max} (min.)
	Thickness (")	Weight (g.)			
H	0.015	3.75	331	95.5	4.75
	0.020	3.90	354	98.0	4.75
	Average		343	96.8	4.75
4-Cl	0.029	4.90	440	154.5	3.25
	0.022	4.60	469	156.5	3.25
	Average		455	155.5	3.25
4-CH ₃	0.024	4.15	279	56.5	5.25
	0.018	3.05	242	81.5	4.50
	Average		261	69.0	4.88

TABLE X

RESULTS OF ELECTRICAL TESTS FOR POLY(ARYLOXYPHOSPHAZENE) HOMOPOLYMERS
 $[(RC_6H_4O)_2PN]_n$

Poly.(R) Samp.No.	Sample Thick. (mils)	ASTM-D143		ASTM-D150					
		Bkdown. Volt. (KV)	Dielec. Strength (V/mil)	Test Frequency			10 ⁶ Hz		
				100 Hz		Power Fact.	10 ³ Hz		Power Fact.
				Dielec. Const.	Power Fact.		Dielec. Const.	Power Fact.	Dielec. Const.
H 1880-06	89	37.0	416	3.47	0.0040		3.45	0.0058	3.28
	85	25.0	294	3.47	0.0036		3.44	0.0058	3.28
	92	29.0	315	3.46	0.0042		3.43	0.0056	3.26
Average	89	30.0	342	3.47	0.0039		3.44	0.0057	3.27
3-CH ₃ 1847-30	114	47.0	412	3.55	0.011		3.51	0.0066	3.17
	91	22.0	242	3.59	0.010		3.54	0.0069	3.49
	102	42.0	412	3.49	0.010		3.57	0.0065	3.23
Average	102	37.0	355	3.54	0.010		3.54	0.0067	3.30
4-Cl 1863-30	79	35.0	443	3.14	0.0044		3.12	0.0035	3.08
	80	31.0	388	3.11	0.0047		3.08	0.0036	3.04
	66	21.0	318	3.09	0.0043		3.07	0.0033	3.03
Average	75	29.0	383	3.11	0.0045		3.09	0.0035	3.05

4.0 MATERIALS SUPPLIED FOR EVALUATION

Materials which were supplied to NAVSEC for further evaluation by various Navy laboratories are given in Table XI. A large number of tests and evaluations will be conducted with these poly(aryloxyphosphazenes), but results are not yet available. Tests will include a determination of smoke and toxicity, foam properties and adhesive characteristics for selected polymers. Small quantities (5 g.) of these samples also were supplied to AMMRC for their study.

TABLE XI

POLY(ARYLOXYPHOSPHAZENES) SUPPLIED FOR EVALUATION

<u>Compound</u>	<u>Sample No.</u>	<u>Quantity</u>
$[(C_6H_5O)_2PN]_n$	1880-20	2.2 lbs.
$[(4-ClC_6H_4O)_2PN]_n$	1863-08	2.2 lbs.
$[(3-CH_3C_6H_4O)_2PN]_n$	1847-30	1.0 lb.
$[(3-CH_3C_6H_4O)_2PN-(4-CH_3C_6H_4O)_2PN]_n$ (3:2)	1962-10	1.0 lb.
$[(C_6H_5O)_2PN-(4-C_2H_5C_6H_4O)_2PN]_n$	1847-46	1.0 lb.
$[(4-ClC_6H_4O)_2PN-(2,4-Cl_2C_6H_3O)_2PN]_n$	1829-50	45 grams

5.0 DISCUSSION

The program proceeded through several stages which included the development of appropriate synthesis techniques, characterization, and large scale preparations for further evaluation. Procedures in synthesis were evolved which afforded a variety of completely substituted, tractable, high molecular weight poly(aryloxyphosphazenes). Isolation and purification was simplified until a relatively simple operation gave pure product. Concurrently, equipment for flame-retardancy tests was constructed. Then, the poly(aryloxyphosphazenes) were prepared in sufficient quantity to be tested for flame-retardancy and electrical properties. Many of the most promising candidates were prepared in 1-2.2 pound quantities for evaluation by Naval laboratories.

The syntheses of completely substituted poly(aryloxyphosphazenes) required much higher reaction temperatures (125-135°C) and longer times (\geq 20 hours) than the preparation of poly(alkoxy- or fluoroalkoxyphosphazenes) [Ref. 4, 8]. This reduced reactivity may be related to the basicity of the sodium aryloxides and/or to their large size (steric effects).

Generally, 10-15% excess aryloxide over P-Cl equivalents and 10% excess alcohol over sodium was employed in the preparation of homopolymers and copolymers. Any trace of water in the resultant aryloxide solutions was removed by a benzene azeotrope and sufficient benzene was removed to achieve the required reaction temperature. The simplified purification of the plastics required only water or water/methanol slurry techniques to give pure products.

Preparations carried out at 95°C gave materials which contained relatively large amounts of chlorine. This result is contradictory to published reports [Ref. 9, 10] concerning the preparation of these materials. Allen et. al. [Ref. 10] claimed to have obtained completely substituted $[(4\text{-ClC}_6\text{H}_4\text{O})_2\text{PN}]_n$ and $[(2,4\text{-Cl}_2\text{C}_6\text{H}_3\text{O})_2\text{PN}]_n$ homopolymers with a reaction temperature of about 70°C and a 48 hour reaction time. Absolutely no data was presented which would support the contention of complete substitution (elemental analyses, solubilities, NMR, etc.). In view of the temperatures which we found to be necessary to lead to complete substitution (including $[(4\text{-ClC}_6\text{H}_4\text{O})_2\text{PN}]_n$, rationalization of these results is difficult. Furthermore, we were unable to prepare tractable $[(2,4\text{-Cl}_2\text{C}_6\text{H}_3\text{O})_2\text{PN}]_n$. Without additional supportive evidence, the materials prepared by Allen et. al. are presumed to be copolymers which contain large amounts of P-Cl bonds.

Complete substitution of chlorine is essential to prepare polymers whose composition is specific and reproducible for physical and mechanical property studies. The presence of small amounts of backbone chlorine would increase flame-retardancy, but hydrolytic instability with attendant generation of corrosive by-product(s) and thermal instability probably would result.

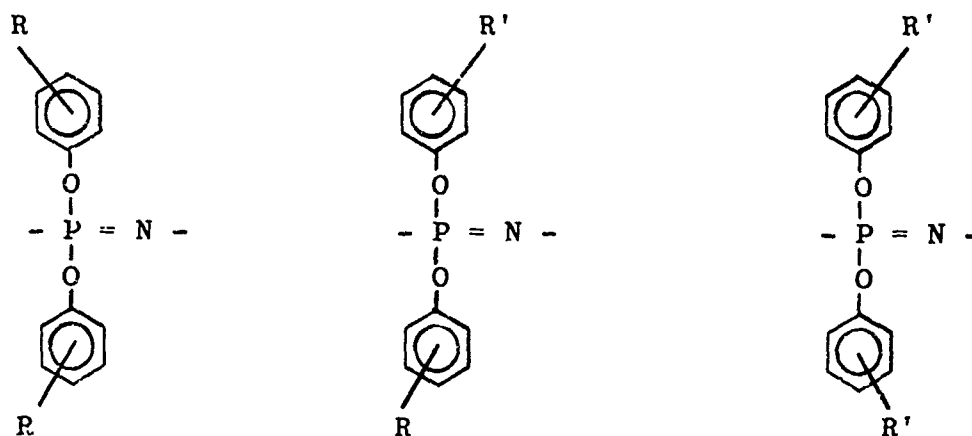
The procedures described above afforded completely substituted homopolymers and copolymers when the aryloxides had a group in the 3- or 4- position. However, completely substituted poly(aryloxyphosphazene) homopolymers which contained a group in the 2- position could not be prepared under the same reaction conditions. This difficulty was discovered when several preparations of the $[(2,4\text{-Cl}_2\text{C}_6\text{H}_3\text{O})_2\text{PN}]_n$ homopolymer failed. This homopolymer was sought because a knowledge of its properties was desired and because a very high LOI (> 65) was anticipated.

Therefore, a study of the feasibility of the preparation of a completely substituted homopolymer with any substituent other than hydrogen in the 2- position was undertaken. Two phenols, one with a substituent which activated the aryloxy-ring and one with a substituent which deactivated the ring relative to $\text{C}_6\text{H}_5\text{O-}$, were investigated. The resultant homopolymers, $[(2\text{-CH}_3\text{C}_6\text{H}_4\text{O})_2\text{PN}]_n$ and $[(2\text{-ClC}_6\text{H}_4\text{O})_2\text{PN}]_n$, were obtained as incompletely substituted materials, but their preparation may be possible. The use of higher reaction temperatures or solvents which promote reaction may prove successful.

For the most part two solvents were used during this program for the preparation of sodium aryloxides, bis(2-ethoxyethyl)ether and bis(2-methoxyethyl)ether (diglyme). When discrepancies in elemental analysis of several homopolymers prepared in distilled bis(2-ethoxyethyl)ether were discovered, more stringent purification procedures were implemented. The more highly purified solvent appeared to solve the problem. Now, bis(2-methoxyethyl)ether is considered the solvent of choice because it is commercially available in high purity and it is a better solvent for most aryloxides.

The preparative sequence (see p. 2) shown in the equations (1) and (2) makes the rapid preparation of whole families of poly(phosphazenes) much more facile than is possible in conventional polymer preparations (addition or condensation polymerizations). The latter techniques most often require different reaction conditions for each new polymerization which is conducted rather than utilization of the same polymerization condition for each polyphosphazene preparation.

When a mixture of alkoxides is used for the preparation of copolymers as shown earlier in equation (2), substitution occurs in a nonregular fashion and a copolymer which contains the units depicted below is obtained.



The preparation of poly(aryloxyphosphazene) copolymers was highly desirable for a variety of reasons. Some copolymers would be expected to be elastomeric, while others were expected to have advantages with respect to flame retardancy, processability, or cost.

The preparation of poly(aryloxyphosphazene) homopolymers which were elastomeric was not possible (several other derivatives not reported herein were prepared for another program). Properly selected choices of substituents to form poly(aryloxyphosphazene) copolymers did produce elastomers. However, the one elastomer which was prepared and which had a satisfactory LOI $\{[(C_6H_5O)_2PN-(4-C_2H_5C_6H_4O)_2PN]_n, LOI = 27\}$ was somewhat leathery and had a relatively high T_g ($\sim 27^\circ C$).

As detailed above, the preparation of homopolymers which contained chlorine in the 2- position on the aryloxy- ring was

unsuccessful. Almost all inexpensive polyhalophenols contain the second halogen substituent in the 2- position and this circumstance could limit the ability to prepare very high LOI poly(haloaryloxyphosphazenes). However, the preparation of poly(aryloxyphosphazene) copolymers allowed the introduction of at least some quantity of highly halogenated aryloxy-substituents (2,4- positions) onto the backbone. The preparation of tractable 1:1 compositions of the $[(4-\text{ClC}_6\text{H}_4\text{O})_2\text{PN}-(2,4-\text{Cl}_2\text{C}_6\text{H}_3\text{O})_2\text{PN}]_n$ and the $[(\text{C}_6\text{H}_5\text{O})_2\text{PN}-(2,4-\text{Cl}_2\text{C}_6\text{H}_3\text{O})_2\text{PN}]_n$ copolymers was accomplished while the preparation of a tractable 1:3 composition of $[(4-\text{ClC}_6\text{H}_4\text{O})_2\text{PN}-(2,4-\text{Cl}_2\text{C}_6\text{H}_3\text{O})_2\text{PN}]_n$ was not successful.

The inexpensive $[(4-\text{CH}_3\text{C}_6\text{H}_4\text{O})_2\text{PN}]_n$ and $[(3-\text{CH}_3\text{C}_6\text{H}_4\text{O})_2\text{PN}]_n$ homopolymers were prepared from the respective isomerically pure alcohols. However, a much less expensive mixture of the two alcohols $[(60(3-\text{CH}_3\text{C}_6\text{H}_4\text{OH}):40(4-\text{CH}_3\text{C}_6\text{H}_4\text{OH})]$ is commercially available, and a $[(3-\text{CH}_3\text{C}_6\text{H}_4\text{O})_2\text{PN}-(4-\text{CH}_3\text{C}_6\text{H}_4\text{O})_2\text{PN}]_n$ copolymer was prepared from this mixture of alcohols. The copolymer was a softer plastic than either homopolymer.

With the exception of the $[(\text{C}_6\text{H}_5\text{O})_2\text{PN}-(4-\text{C}_2\text{H}_5\text{C}_6\text{H}_4\text{O})_2\text{PN}]_n$ copolymer, all the polymers were obtained as plastics. This copolymer was a leathery elastomer. The plastics were found to be excellent film formers.

Without a doubt, the most successful development of this program was the demonstration that a rather extensive family of flame-retardant poly(aryloxyphosphazenes) could be prepared. Thin films of all polymers prepared, which included the elastomeric $[(\text{C}_6\text{H}_5\text{O})_2\text{PN}-(4-\text{C}_2\text{H}_5\text{C}_6\text{H}_4\text{O})_2\text{PN}]_n$ copolymer, were self-extinguishing when withdrawn from a gas/oxygen flame. This qualitative measure of flame-retardancy was confirmed upon more definitive flame-retardancy tests such as the Hooker Laboratory Intermittent Test (HLT-15), ASTM D229 test, and particularly the Limiting Oxygen Index.

The HLT-15 is a measure of degree of flame-retardancy when a specimen of fixed dimensions is placed vertically over a controlled flame and withdrawn and returned several times at varying time intervals. The maximum rating possible is 100 which was achieved by $[(4-\text{CH}_3\text{C}_6\text{H}_4\text{O})_2\text{PN}]_n$, $[(4-\text{ClC}_6\text{H}_4\text{O})_2\text{PN}]_n$, and $[(4-\text{ClC}_6\text{H}_4\text{O})_2\text{PN}-(2,4-\text{Cl}_2\text{C}_6\text{H}_3\text{O})_2\text{PN}]_n$. Because the former homopolymer which was one of our most flammable compositions gave the maximum rating, the test was not performed on the other polymers prepared during this program.

The Limiting Oxygen Index (ASTM D2863) is one of the most reproducible and definitive of the great variety of

flame-retardancy tests that have been developed to date. A sample bar held vertically is ignited from the top in a glass cylinder under a fixed volume flow in a predetermined oxygen-nitrogen mixture. The test measures the minimum concentration of oxygen necessary to maintain combustion at a defined burning rate.

As shown in Table VII, unfilled and uncured poly(alkyl-aryloxyphosphazene) homopolymers and copolymers had ratings of 27-28 and the $[(C_6H_5O)_2PN]_n$ homopolymer had a rating of 33. As anticipated, the halogenated poly(aryloxyphosphazenes) had significantly higher LOI values of 38-65 with bromine more effective than chlorine. Interestingly, the $[(4-ClC_6H_4O)_2PN]_n$ homopolymer and $[(C_6H_5O)_2PN-(2,4-Cl_2C_6H_3O)_2PN]_n$ (1:1) copolymer which have identical chlorine content gave essentially identical LOI values (43-44). However, the LOI for the $[(3-ClC_6H_4O)_2PN]_n$ homopolymer was 51. This difference must be related to differences in combustion rate and/or combustion mechanism of a 3-chloroaryloxy group versus the 4-chloroaryloxy group. By comparison, LOI values for several commercial polymers are given in Table XII [Ref. 10, 11, 12].

TABLE XII
LIMITING OXYGEN INDEX OF COMMERCIAL PLASTICS

<u>Polymer</u>	<u>LOI</u>
Poly(aryloxyphosphazene)	27-65
Polyethylene	17.4
Polystyrene	18.3
Polyester	20.6
Nomex (trademark of Du Pont)	26.7
Nylon 6-6	28.7
Durette (trademark of Monsanto)[Ref. 12]	37.0
Polyvinylidene fluoride	43.7
Polyvinyl chloride	47.0

These LOI comparisons strongly indicate that the poly(halo-aryloxyphosphazenes) are vastly superior in flame-retardancy to the majority of common, commercial plastics.

Several unfilled, uncured poly(aryloxyphosphazenes) were tested according to the National Electrical Manufacturers Test (ASTM D229) which was designed to evaluate rigid plastics as insulation for electrical applications. The test involves a sample bar placed vertically in a metal coil that is heated to 860°C (1580°F) and ignited by sparks from a pair of electrodes. The time to ignition (T_i) and the burning time (T_b) after de-energizing are measured. The poly(aryloxyphosphazenes) which were tested followed the same order for aryloxy substituents found for the LOI test, i.e., 4-Cl>>H>3-CH₃. A comparison of the poly(aryloxyphosphazenes) with glass-loaded polyester and epoxy resins [Ref. 13] are shown in Table XIII.

TABLE XIII
COMPARISON OF VARIOUS POLYMERS ACCORDING TO ASTM D229

Polymer	% Glass	Ignition Time (T_i , sec.)	Burn Time (T_b , sec.)
$[(C_6H_5O)_2PN]_n$	0	115	51
$[(3-CH_3C_6H_4O)_2PN]_n$	0	83	52
$[(4-ClC_6H_4O)_2PN]_n$	0	136	4.5
GR-941*	35	67	732
GR-941* (5% $[Cl_2PN]_n + 1.8 Sb_2O_3$)	60	71	712
GR-684**	40	51	111
Hetron 355**	60	79	28
Epon 828 (5% $[Cl_2PN]_n$)	25	51	107
Epon 828 (5% $[Cl_2PN]_n$)	40	62	135

* Non-fire-resistant polyester [Ref. 13]

** Fire-resistant commercial polyester; 355 contained Sb_2O_3 (5%)

Another important consideration in the selection of flame-retardant materials is the generation of smoke and toxic gases during combustion. These by-products obscure vision and disrupt normal respiratory processes. Most conventional polymeric materials are not sufficiently fire-retardant and are formulated with fire-retardant additives. These additives generally increase the problem of excessive development of smoke and corrosive gases.

Results of the NBS Smoke Density Chamber Test on unfilled, uncured poly(aryloxyphosphazenes) are quite encouraging. A comparison with several commercial plastics [Ref. 7] is presented in Table XIV.

Although polystyrene has a favorably low maximum rate, its maximum density value is higher than values found for the poly(aryloxyphosphazenes). The $[(3\text{-CH}_3\text{C}_6\text{H}_4\text{O})_2\text{PN}]_n$ homopolymer had the best combination of low D_{max} and low rate of combustion.

TABLE XIV
NBS Smoke Density Values for Polymers

Polymer	Max. Smoke Density (D_{max})	Max. Rate (min.) of Smoke Density
$[(\text{C}_6\text{H}_5\text{O})_2\text{PN}]_n$	343	96.8
$[(3\text{-CH}_3\text{C}_6\text{H}_4\text{O})_2\text{PN}]_n$	261	69.0
$[(4\text{-ClC}_6\text{H}_4\text{O})_2\text{PN}]_n$	455	155.5
Polystyrene	470	2
FR Acrylic UV-Abs	480	151
Polyvinylchloride, rigid	525	195

Presently, little is known about the nature of the smoke emitted when a polyphosphazene burns. When linear $[\text{Cl}_2\text{PN}]_n$ was used as an additive for polyesters [Ref. 13], no adverse effect on either particulates or carbon monoxide content was observed. Our materials were submitted to the Naval Ship Engineering Center for evaluation of smoke density and toxicity and combustion products, but the results are not yet available.

The potential of poly(aryloxyphosphazenes) for use as fire-retardant coverings and encapsulating materials for electrical components also was evaluated briefly. The unfilled and uncured test specimens were fabricated in a very rudimentary manner and little effort was made to optimize molding conditions or to take precautions concerning moisture entrapment, etc. The polymers were quite polydisperse and small amounts of cyclic or low molecular weight linear poly(aryloxyphosphazenes) could only be detrimental to electrical properties.

Electrical properties are compared with values for electrical grades of polyvinyl chloride and polyethylene [Ref. 14] in Table XV. The power factor for the poly(aryloxyphosphazenes) was reasonably constant over the entire frequency range tested. They had a dissipation factor which was lower than PVC but higher than PE.

Further investigations in two important areas should be carried out. Control of molecular weight and determination of accurate values for T_m were not addressed sufficiently during the course of this program. The difficulties are detailed below.

A sample of $[(4-\text{ClC}_6\text{H}_4\text{O})_2\text{PN}]_n$, which had an intrinsic viscosity of 1.4 dl./g., was examined by vapor phase osmometry and light scattering (at AMMRC). Values for \bar{M}_n and \bar{M}_w were 2.2×10^5 and 2.1×10^6 , respectively. Data have not been obtained for other materials, but all poly(aryloxyphosphazenes) are expected to be similarly polydisperse. Almost certainly, these high molecular weight ranges and polydispersities are less than ideal (must be reduced) for ease in processing and for development of optimum physical properties in plastics.

Values for T_m for the poly(aryloxyphosphazenes) are not contained in this report because some confusion exists as to the true values. Observation of samples under polarized light on a hot-stage microscope (PLHM) gave no loss of birefringence up to 227°C with two exceptions. By Differential Thermal Analysis (DTA) several samples showed sharp peaks in the 130-150°C range, but these endothermic absorptions generally did not correlate with the PLHM observations. Furthermore, most of the poly(aryloxyphosphazenes) undergo plastic flow under low pressure (T_s) around 100°C. Many of the polymers were molded to give satisfactory specimens but other moldings were not satisfactory. These phenomena require further study because they have implications for processing and use temperatures of the materials.

TABLE XV

COMPARISON OF ELECTRICAL PROPERTIES OF SEVERAL PLASTICS

Polymer	Dielectric Constant			Dissipation Factor			Dielectric Strength (v./mil.)
	Frequency Tested			Frequency Tested			
	100 Hz	10 ³ Hz	10 ⁶ Hz	100 Hz	10 ³ Hz	10 ⁶ Hz	
[(C ₆ H ₅ O) ₂ PN] _n	3.47	3.44	3.27	0.0039	0.0057	0.012	337
[(3-CH ₃ C ₆ H ₄ O) ₂ PN] _n	3.54	3.54	3.30	0.010	0.0067	0.038	363
[(4-ClC ₆ H ₄ O) ₂ PN] _n	3.11	3.09	3.05	0.0045	0.0035	0.001	387
	60 Hz			60 Hz			
Polyethylene (wire and cable grade)	2.28-7.60	2.27-7.40	-	0.003-0.044	0.0048-0.0490	-	230-1420
Polyvinyl chloride (flexible)	5.0-9.0	4.0-8.0	3.3-4.5	0.08-0.15	0.07-0.16	0.04-0.44	300-1000
Polyvinyl chloride (rigid)	3.2-3.6	3.0-3.3	2.3-3.1	0.007-0.020	0.009-0.017	0.006-0.019	425-1300

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